

PATENT

APPLICATION FOR UNITED STATES LETTER PATENT

FOR

IONIC LIQUIDS CONTAINING A SULFONATE ANION

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2 **IONIC LIQUIDS CONTAINING A SULFONATE ANION**

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4 **RELATED APPLICATION DATA**

5 **[0001]** The present application claims priority to U.S. Provisional Application No.
6 60/404,178, filed August 16, 2002 and U.S. Provisional Application No. 60/404,202, filed
7 August 16, 2002.

8 **FIELD OF THE INVENTIONS**

9 **[0002]** The present inventions pertain to compositions comprising an ionic liquid
10 comprising a Docusate anion, a docusate variant anion, or other sulfonate anion, and processes
11 for making said compositions.

12 **BACKGROUND AND SUMMARY OF THE INVENTIONS**

13 **[0002]** Ionic liquids are salts that are liquid at ambient or near ambient temperatures. Ionic
14 liquids have a number of uses that include replacing organic solvents in chemical processes and
15 reactions, extracting organic compounds from aqueous waste streams, and as electrolytes in
16 devices such as capacitors and batteries. This is because, unlike conventional organic solvents,
17 ionic liquids are non-volatile and non-flammable. These properties are advantageous to help
18 reduce losses to evaporation, eliminate volatile organic emissions, and improve safety.

19 **[0003]** Other properties of ionic liquids have also proved advantageous. For example, many
20 ionic liquids have a broad temperature range at which they remain liquid and also are stable over
21 a broad pH range. This is beneficial for high temperature processes with a demanding pH.
22 Further, some ionic liquid systems can be used as both a solvent and catalyst. For example,
23 [bmim]-Al₂Cl₇ and [emim]-Al₂Cl₇ can be employed as a solvent and catalyst in Friedel-Crafts
24 reactions wherein bmim is 1-butyl-3methylimidazolium and emim is 1-ethyl-3-
25 methylimidazolium.

26 **[0004]** For the aforementioned reasons, it would be desirable to discover new ionic liquid
27 compounds with advantageous properties. It would further be desirable if such compounds could
28 be made by simple processes with low amounts of waste and impurities.

29 **[0005]** Advantageously, new ionic liquid compounds have been discovered. The compounds
30 comprise either a docusate or other sulfonate anion and are made via simple processes that are
31 capable of producing ionic liquids having a high purity.

1 **DETAILED DESCRIPTION OF THE INVENTIONS**

2 [0006] As used herein "ionic liquid" means a salt comprising a cation and an anion. The salt
3 (or hydrate or solvate of the salt) is a liquid at ambient or near ambient temperatures (i.e., having
4 a melting point, or melting range, less than about 100° C). An ionic liquid may comprise two or
5 more different salts, e.g., mixtures of salts comprising two or more different cations, anions, or
6 both. The ionic liquids of the present inventions are often hydrated or solvated. Thus, both
7 hydrates and solvates are considered to be within the definition of "ionic liquid."

8 [0007] As used herein "hydrophilic ionic liquid" means an ionic liquid which is partially or
9 wholly miscible with water.

10 [0008] As used herein "hydrophobic ionic liquid" means an ionic liquid which is relatively
11 immiscible with water, i.e., forms two phases at ambient conditions.

12 [0009] As used herein "composition" includes a mixture of the materials that comprise the
13 composition, as well as, products formed by the reaction or the decomposition of the materials
14 that comprise the composition.

15 [0010] As used herein "derived from" means made or mixed from the specified materials,
16 but not necessarily composed of a simple mixture of those materials. Substances "derived from"
17 specified materials may be simple mixtures of the original materials, and may also include the
18 reaction products of those materials, or may even be wholly composed of reaction or
19 decomposition products of the original materials.

20 [0011] As used herein "halo" means chloro, bromo, fluoro, or iodo, arylene means a divalent
21 aromatic group such as phenylene, naphthylene, biphenylene, antracenylene,
22 phenanthrenylene, etc., heteroarylene means a divalent heteroaromatic group such as pyrrolene,
23 furanylene, thiophenylene, pyridinylene, etc., alkylene means a divalent alkane group which may
24 be substituted with one or more heteroatoms such as nitrogen or oxygen, cycloalkylene means a
25 divalent cycloalkane group which may be substituted with one or more heteroatoms such as
26 nitrogen or oxygen, alkenylene means a divalent alkene group which may be substituted with
27 one or more heteroatoms such as nitrogen or oxygen.

28 [0012] As used herein "Docusate" is the anion of the bis(2-ethylhexyl)ester of sulfosuccinic
29 acid. The chemical formula of Docusate (anion) is $C_{20}H_{37}O_7S^-$. As used herein, "docusate
30 variant" is taken to include the compounds described by chemical structures I and III described

1 below and includes the anions of bis(organo)ester derivatives of sulfosuccinic acid and anions of
2 bis(organoamide) derivatives of sulfosuccinic acid.

3 [0013] Any numerical values recited herein include all values from the lower value to the
4 upper value in increments of one unit provided that there is a separation of at least 2 units
5 between any lower value and any higher value. As an example, if it is stated that the amount of a
6 component or a value of a process variable such as, for example, temperature, pressure, time and
7 the like is, for example, from 1 to 90, preferably from 20 to 80, more preferably from 30 to 70, it
8 is intended that values such as 15 to 85, 22 to 68, 43 to 51, 30 to 32 and the like, are expressly
9 enumerated in this specification. For values which are less than one, one unit is considered to be
10 0.0001, 0.001, 0.01 or 0.1 as appropriate. These are only examples of what is specifically
11 intended and all possible combinations of numerical values between the lowest value and the
12 highest value enumerated are to be considered to be expressly stated in this application in a
13 similar manner.

14 [0014] The ionic liquid of the present invention comprise one or more compounds. Thus, the
15 ionic liquid may be a pure compound or may be a mixture of compounds. Each compound
16 comprises an anion or a mixture of anions and a cation or a mixture of cations as described
17 below.

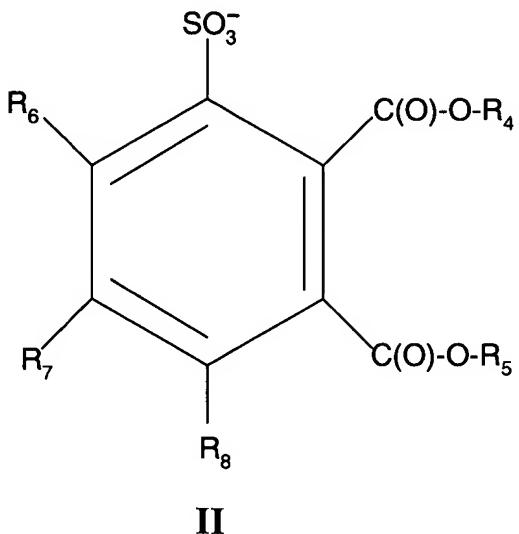
18 Anions

19 [0015] Exemplary anions of compounds of the instant invention include those having a
20 chemical structure selected from



I

1 [0016] R_1, R_2, R_4 and R_5 in Structure I and II above are independently selected from the
2 group consisting of substituted or unsubstituted alkyl or alkenyl groups. The alkyl or alkenyl



3 groups of R_1, R_2, R_4 and R_5 should have a sufficient number of carbon atoms so that the ionic
4 liquid has the desired properties. For example, if a hydrophobic ionic liquid is desired then the
5 total number of carbon atoms in the ionic liquid will typically be more than if a hydrophilic ionic
6 liquid is desired. However, if there are too many carbon atoms in the anion then the ionic liquid
7 may be less useful as an ionic liquid due to a decline in properties such as vapor pressure, dipole
8 moment, polarity, etc.

9 [0017] For hydrophobic ionic liquids R_1, R_2, R_4 and R_5 are preferably independently selected
10 from alkyl groups having about five or more carbon atoms, preferably from about six to about
11 eighteen carbon atoms. One preferable group for R_1, R_2, R_4 and R_5 is
12 $-\text{CH}_2-\text{CH}(\text{CH}_2\text{CH}_3)(\text{CH}_5\text{CH}_2-\text{CH}_3)$. This group is useful for the properties it gives to the ionic
13 liquid and for its cost and convenience to manufacture.

14 [0018] R_3 in structure I above is a substituted or unsubstituted alkylene group, heteroarylene
15 group, arylene group, or cycloalkylene group. Preferably R_3 is a substituted or unsubstituted
16 alkylene group and even more preferably R_3 is $-(\text{CH}_2)_n-$ wherein n is an integer of from about
17 one to about 10.

18 [0019] R_6, R_7 , and R_8 are independently selected from hydrogen (H) or another substituent
19 such as, for example, alkyl, NO_2 , halo, cyano, silyl, and OH. Preferably, R_6, R_7 , and R_8 are H.

1 [0020] In some instances, two or more adjacent substitutents such as or R₁ and R₂, R₄ and R₅,
2 R₆ and R₇, and/or R₇ and R₈ may be taken together to form a ring such as a 5-7 membered
3 carbocyclic ring. Examples of such carbocyclic rings include cyclopentyl and cyclohexyl rings.

4 [0021] R₁, R₂, R₃, R₄, R₅, R₆, R₇, and R₈ may optionally be substituted with one or more
5 substituents. The type of the substituent is not particularly critical so long as the compound or
6 mixture of compounds has the desired ionic liquid properties. Thus, the substituents usually
7 include typical and non-typical organic substituents such as those selected from the group
8 consisting of alkyl, NO₂, halo, cyano, silyl, OH, and other suitable substituents. The substituent
9 group itself may often be further branched.

10 [0022] Another exemplary anion that can be used to make ionic liquids is a docusate variant
11 having the following chemical structure:



III

12

13

14 [0023] R₁, R₂, R₃, R₄, and R₅ in chemical structure III can be independently selected from a
15 hydrogen atom (H) or a carbon-containing group, e.g., alkyl, alkenyl, alkynyl, aryl, benzyl, alkyl-
16 ether, etc.

17 [0024] In an embodiment, the anion source is a sodium salt of the 2-ethylhexyl amide
18 sulfonate salt, which can be synthesized using known techniques having the benefit of this
19 Specification. For example, an anion was prepared having the above chemical structure III with
20 R₁ and R₅ each being a 2-ethylhexyl group, R₂ and R₄ each being a hydrogen atom, and R₃ being
21 a methylene group. Two different ionic liquids were prepared using this anion by first isolating
22 it as a sodium salt and then reacting it with a source of two different cations. The cation in one
23 of the ionic liquids was tetrabutylammonium cation. The cation in the other ionic liquid was 1-
24 methyl-3-hexyl imidazolium.

25 [0025] In other experiments, a second anion was prepared having the above chemical
26 structure III with R₁ and R₅ each being a 2-ethylhexyl group, R₂ and R₄ each being an ethyl
27 group, and R₃ being a methylene group. Two more ionic liquids were prepared using this anion
28 by first isolating it as a sodium salt and then (in separate experiments) reacting it with a source of

1 the same two cations mentioned above, namely tetrabutylammonium cation and 1-methyl-3-
2 hexyl imidazolium.

3 [0026] Based upon experiments in which ionic liquids have been made from anions having
4 chemical structure III, it is believed that, as is the case with the docusate salts and their
5 derivatives and variants, each of the R groups in chemical structure III could vary in length or
6 composition and still give rise to an ionic liquid when combined with an suitable cation, e.g., an
7 onium cation.

8 Cations

9 [0027] The cation of the ionic liquid to be produced is not particularly critical so long as the
10 ionic liquid has properties to make it suitable for its intended use. Typical useful cations include,
11 for example, "onium" cations. Onium cations include cations such as substituted or
12 unsubstituted ammonium, phosphonium, and sulfonium cations. Preferred onium cations
13 include, for example, substituted or unsubstituted N-alkyl or N-aryl pyridinium, pyridazinium,
14 pyrimidinium, pyrazinium, imidazolium, pyrazolium, thiazolium, oxazolium, triazolium,
15 imidazolinium, methylpyrrolidinium, isothiazolium, isoxazolium, oxazolium, pyrrolium, and
16 thiophenium. The substituents include one or more of the following groups: halo, alkyl, and aryl
17 groups such as phenyl. In addition, two adjacent substituents may be joined together to form an
18 alkylene radical thereby forming a ring structure converging on N. The alkyl, phenyl, and
19 alkylene radicals may be further substituted. Another particularly preferred cation is an
20 ammonium cation substituted by one or more groups such as alkyl and aryl groups such as
21 phenyl. Many such cations and substituted cations are described in U.S. Patent Nos. 5,827,602
22 and 5,965,054, which are incorporated by reference in their entirety.

23 [0028] Other suitable cations include BMIM, tetrabutyl ammonium, tributylmethyl
24 ammonium, tetrabutyl phosphonium, tetraethyl ammonium, N, N - dialkyl pyrrolidinium,
25 trimethyl 2-hydroxyethyl ammonium, N, N' - dialkyl imidazolium, N-alkylpyridinium, or
26 mixtures thereof. The cation may be an onium cation and optionally contains more than 4
27 carbon atoms.

28 Processes to make Compounds Having Structures I-III and Mixtures Thereof

29 [0029] The ionic liquid compounds of structures I-II may be conveniently made by a number
30 of different processes. One process which is suitable for making hydrophobic or hydrophilic
31 ionic liquids or mixtures of the present invention comprises using metathesis, i.e., a double

1 decomposition reaction, whereby the reaction of two or more compounds forms two or more new
2 compounds – one of which is the ionic liquid. For example, reacting [bmim]Cl with sodium
3 docusate will yield [bmim]docusate and NaCl. The two or more compounds produced by the
4 metathesis reaction can then be separated by any means.

5 [0030] The manner of contacting the two or more compounds to form the ionic liquid is not
6 particularly important so long as the desired reaction occurs. Generally, the compounds can be
7 mixed in any order, can be formed *in situ*, or can be mixed together with a solvent such as water
8 which is at least partially miscible and does not significantly react with any of the compounds.

9 [0031] The starting compounds are often readily available and, in addition, many syntheses
10 are available to those skilled in the art to make the desired starting compounds. The mixing
11 conditions may vary depending on the specific compounds employed and the desired product. In
12 most instances, it is acceptable to contact the compounds and an optional solvent such as water
13 or dichloromethane at ambient pressure and a temperature high enough for the reaction to occur
14 efficiently but not so high as to decompose or boil off any starting compound. Generally, the
15 contacting temperature may range from about 75 to about 110 °C, preferably from about 85 to
16 about 100 °C. When water is used as a solvent, temperatures of about 75 to about 110 °C are
17 sometimes preferable because this tends to breaks up emulsions which typically form between
18 the ionic liquid and water. On the other hand, when the solvent is organic (e.g.,
19 dichloromethane), the preferred temperature is typically substantially lower, usually around room
20 temperature, e.g., 25 °C or slightly above room temperature.

21 [0032] The manner in which the increased temperature is achieved and maintained is not
22 particularly critical. Often any heating element may be employed as the compounds are mixed
23 or the starting compounds can be heated separately and then mixed. Similarly, any vessel or
24 reactor can be employed so long as it is of adequate size and material. Often it is beneficial to
25 employ a stirring means to facilitate the reaction.

26 [0033] Generally, the increased temperature is maintained for at least a sufficient time until
27 the desired reaction has occurred to the desired extent. In some instances, it may be desirable to
28 maintain the increased temperature for a longer time than it takes to complete the reaction. In
29 this manner, any water or lower boiling components that are formed as byproducts or present as
30 solvents can be removed by boiling.

1 [0034] The amount of each of the starting compounds may vary depending upon the desired
2 yield. In general, high yields are often obtained by using about the stoichiometric amount of
3 reactants, i.e., about a 1:1 ratio. However, as one skilled in the art will appreciate, different
4 reaction conditions may alter the ratio of reactants at which the optimum yield occurs.

5 [0035] If one desires to make an ionic liquid mixture comprising two or more different salts,
6 then it can be accomplished by employing a mixture of three or more different compounds so
7 that a variety of salts are formed. The resulting ionic liquid salt mixture can then be used as a
8 mixture or, if desired, individual salts can be separated by routine means.

9 [0036] If necessary, the ionic liquid or ionic liquid mixture may be recovered from the
10 solvent and/or reaction mixture by any suitable means the most efficient of which may vary
11 depending upon the type and desired purity of the ionic liquid or mixture. Suitable means of
12 recovery include rotary evaporation or distillation, azeotropic distillation, ion chromatography,
13 liquid liquid extraction, crystallization, pervaporation, drying agents, and reverse osmosis.

14 [0037] While the aforementioned process may be employed to make hydrophobic or
15 hydrophilic ionic liquids, in some applications it is preferable to make hydrophobic ionic liquids.
16 This is because hydrophobic ionic liquids are often not very soluble in the water which is often
17 used as a reaction medium. Therefore, simple liquid-liquid extraction can be used to separate the
18 hydrophobic ionic liquid from the soluble byproduct. In contrast, hydrophilic ionic liquids are
19 often miscible with the byproduct. Consequently, a different separation method, e.g., solvent
20 extraction, can be employed. For example, it may be desirable or necessary to use a hydrophobic
21 solvent like an alkyl chloride, e.g. methylene chloride, to extract the ionic liquid.

22 Characteristics and Uses of Ionic Liquids of the Present Invention

23 [0038] The purity of ionic liquids produced by the processes of this invention can often be
24 greater than 55%, preferably greater than 60%, more preferably greater than 70%, most
25 preferably greater than 80%. This is often advantageous for processes that require high purity
26 materials such as in the electronics industry. The ionic liquids are also preferably hydrophobic
27 and thus useful in many processes as a substitute for an organic solvent and in mixtures with
28 catalysts such as ZnCl₂, CuCl₂, AlCl₃, and organic catalysts.

29 [0039] The ionic liquids of the present invention are also often useful in mixtures with
30 hydrocarbons such as alkanes, e.g., hexane. The mixtures often do not hold static electricity
31 charge and thus will not ignite or explode readily.

1 Docusate and Docusate Variants in Supercritical CO₂ Applications

2 **[0040]** It has been found that tetrabutylammonium docusate is soluble in supercritical carbon
3 dioxide (CO₂). Supercritical applications using CO₂ typically operate at temperatures between
4 above 32° C and pressures above about 1,070 psi. It is believed that the docusate and docusate
5 variant based ionic liquids are useful adjuvants, additives, and detergents for addition to
6 supercritical CO₂ for cleaning, synthesis, and separations applications.

7 Docusate and Docusate Variants as Anti-static Agents

8 **[0041]** It is believed that the docusate and docusate variant based ionic liquids are useful
9 antistatic additives for fuel applications and polymer applications. The docusate and docusate
10 variant based ionic liquids tend to be partially or fully miscible with hydrocarbons (e.g., alkanes
11 such as hexane) and can be added to fuels as anti-static additives. These ionic liquids can also be
12 added to polymers, e.g., polyvinylacetate, as an anti-static additive.

13 Docusate and Docusate Variants in Ionic Liquid Blends

14 **[0042]** In one embodiment, two or more ionic liquids are blended together to form an
15 improved reaction solvent. It is believed that Lewis Acid ionic liquids can be advantageously
16 blended with ionic liquids based upon docusate or docusate variants to form an improved
17 reaction solvent that provides better mixing between reactants to improve reaction kinetics.
18 Because the docusate and docusate variant ionic liquids tend to be at least relatively miscible
19 with the hydrocarbon streams, they tend to inhibit the formation of two phases and improve the
20 mixing and contact between the reactants. Examples of Lewis Acid ionic liquids that are
21 believed to be useful in making blends with the sulfonate anion (e.g., docusate and docusate
22 variant) ionic liquids of the present invention are disclosed in copending U.S. Application
23 entitled "Lewis Acid Ionic Liquids," filed on August 15, 2003 and invented by Roger Moulton
24 (Serial No. currently unknown), which is incorporated by reference as if fully set forth herein.

25 **[0043]** Exemplary Lewis Acid ionic liquids useful in these blends include ionic liquids
26 having (i) a cation selected from ammonium, sulfonium, and phosphonium cations and having
27 less than 14 total carbon atoms; and (ii) an anion having the formula AlyR_{3y+1} wherein y is
28 greater than 0 and R is independently selected from the group consisting of an alkyl group and
29 halogen group. A suitable anion for the Lewis Acid ionic liquid in the blend is aluminum
30 chloride anion.

1 [0044] A suitable cation for the Lewis Acid ionic liquid is tetraalkylammonium. Depending
2 on the desired ionic liquid properties it may be advantageous for one or more of the alkyl groups
3 to be optionally substituted with one or more suitable substituents. Suitable substituents
4 include, for example, halogens such as chloride, bromide, or iodide. Particularly preferred
5 tetralakylammonium cations include trimethylethyl ammonium, trimethyl chloromethyl
6 ammonium, trimethylbutyl ammonium, and tributyl methyl ammonium.

7 [0045] Another suitable cation for the Lewis Acid ionic liquid are the N-alkyl substituted
8 saturated heterocycles such as piperidinium and morpholinium. In particular, piperidinium
9 substituted on the nitrogen with an alkoxy or alkyl group such as –(CH₂)₂OMe, butyl, or propyl
10 are particularly beneficial. Pyrrolidine-based cations can also be employed. The cation may
11 include ether functionality (e.g., NCH₂CH₂OCH₃⁺). The cation may include halogenated alkyl
12 groups.

13 [0046] Exemplary Lewis Acid ionic liquids for the blend include ionic liquids having an
14 aluminum chloride anion and a cation sourced from an ammonium salt such as MeBu₃N Cl,
15 Me₃PentylN Cl, Me₃ButylN Cl, MeEt₃N Cl, Me₂Et₂N Cl, Cl-CH₂-NMe₃ Cl, or N-methyl-N-
16 Butyl Pyrrolidinium Cl. Other exemplary Lewis Acid ionic liquids include N-alkyl substituted
17 piperidinium heptachlorodialuminate, trimethyl chloromethyl ammonium
18 heptachlorodialuminate, trimethylbutyl ammonium heptachlorodialuminate, and tributyl methyl
19 ammonium heptachlorodialuminate.

20 [0047] The following examples are not intended to limit the invention, but rather, are
21 intended only to illustrate a few specific ways the instant invention may be employed.

22 [0048] **Example 1 – Synthesis of tetrabutylammonium docusate**

23 1 mole sodium docusate (444 grams) was dissolved in 2 liters water, and then 1 mole
24 tetrabutylammonium bromide (321 grams) was added as a solid. After stirring for a few
25 minutes, the stirring was stopped and the solution separated into two layers. The top layer was
26 collected in a separatory funnel. It was washed twice with 1 liter of water, and heated to 100 °C
27 to facilitate phase disengagement. The resulting tetrabutylammonium docusate was heated to
28 110 °C to drive off any dissolved water in it. The yield was nearly quantitative (624 grams, 94%
29 yield).

30 [0049] **Examples 2-5**

1 [0050] The ionic liquids of Examples 2-5 in Table 1 below were made substantially as in the
2 same manner as Example 1 except that approximately 1 mole of the starting material in Table 1
3 was substituted for the 1 mole of tetrabutylammonium bromide in Example 1.

4 [0051] **Table 1**

Example	Starting Material	Ionic Liquid	Solubility in water
2	Me(n-Bu) ₃ N Br	Me(n-Bu) ₃ N Docusate	Hydrophobic
3	Me ₃ N(CH ₂) ₆ NMe ₃ Br	Me ₃ N(CH ₂) ₆ NMe ₃ Docusate	Hydrophobic
4	n-Bu ₄ P Br	n-Bu ₄ P Docusate	Hydrophobic
5	Et ₄ N Br	Et ₄ N Docusate	miscible

5 [0052] **Examples 6-10**

6 [0053] The ionic liquids of Examples 6-10 in Table 2 below were made by dissolving
7 sodium docusate in dichloromethane and in a separate flask dissolving the starting material of
8 Table 2 in dichloromethane. The two solutions were mixed and stirred for approximately 12
9 hours. The solutions were then filtered to remove precipitated solid salts, then evaporated to
10 thick syrups. The thick syrups are then extracted with diethyl ether, hexanes or a mixture
11 thereof; again filtering to removed solid salts. After rotary evaporation, the residues are
12 redissolved in hexane/ether and the process of filtration repeated (using progressively smaller
13 fractions of ether in the mix) until no further solids were formed. The resulting salts are then
14 washed with water to effect a final removal of inorganic salts, after which they are dried in
15 vacuo.

16 [0054] **Table 2**

Example	Starting Material	Ionic Liquid
6	1-n-hexyl-3-methyl imidazolium bromide	1-n-hexyl-3-methyl imidazolium docusate
7	1-n-octyl-3-methyl imidazolium bromide	1-n-octyl-3-methyl imidazolium bromide docusate
8	1-n-butyl-3-methyl imidazolium bromide	1-n-butyl-3-methyl imidazolium docusate
9	1-methyl-2-ethyl imidazolium bromide	1-methyl-2-ethyl imidazolium docusate
10	tetra-n-butylammonium bromide	tetra-n-butylammonium docusate

18 [0055] The ionic liquids of Examples 6-10 were generally hydrophobic ionic liquids. In the
19 case of Example 6, 1-hexyl-3-methyl imidazolium docusate, contacting it with 40 volume
20 percent or less of water resulted in the formation of two phases, even after agitation. However,
21

1 when 1-hexyl-3-methyl imidazolium docusate was contacted with 50 volume percent water,
2 agitation produced a stiff, visibly monophasic gel. Addition of additional water to the gel,
3 followed by agitation, resulted in the formation of two phases again. While not wishing to be
4 bound by any particular theory, it is believed that some of the ionic liquids of the present
5 invention may become hydrated or solvated when mixed with some proportions of water. This
6 results in an ionic liquid which is insoluble and forms two phases when mixed with some
7 proportions with water and is a single phase at other proportions. This unique behavior could be
8 very beneficial for some applications in which solubility or insolubility with water is important.

9 **[0056] Example 11**

10 **[0057]** This example details the synthesis of a tetrabutyl ammonium molten salt of the amide
11 having chemical formula III above. One-tenth of a mole (50g) of the sodium salt of the amide-
12 sulfonate salt having chemical structure III above (with R₂ and R₄ being CH₂CH₃, R₁ and R₅
13 each being a 2-ethylhexyl group, and R₃ being CH₂) was dissolved in 250 mL of
14 dichloromethane, and one-tenth mole (32g) of tetrabutyl ammonium bromide was added as a
15 solid. The mixture was stirred for a day, after which time the solution was filtered first through
16 filter paper and then through a short plug of silica gel. The eluted dichloromethane solution was
17 quickly washed with water, dried over magnesium sulfate, and the solvent removed in vacuo,
18 leaving the desired product in high yield (64g, 89%). The product salt is soluble in both water
19 and in several common organic solvents, such as dichloromethane and acetone. The melting
20 range of the resulting salt was less than about 30°C because the product was a viscous oil at room
21 temperature. The product salt included Bis (N-ethyl-N-(2-ethylhexyl)sulfosuccinate diamide)
22 anion paired with tetrabutyl ammonium cation.

23 **[0058] Examples 12-19**

24 **[0059]** These examples detail the preparation of an ionic liquid from a sodium salt of the
25 sulfosuccinate salts, which are docusate variants. The esters were then combined with an onium
26 cation to make an onium molten salt.

27 **[0060]** Ten grams (0.03 mol) of tetrabutylammonium bromide was dissolved in 50 mL of
28 water, and to the stirred solution was added as a solid twelve grams (0.03 mol) of the sodium salt
29 of the di-n-hexyl ester of sulfosuccinic acid. (By “di-n-hexyl ester of sulfosuccinic acid” it is
30 meant that the sulfosuccinic acid molecule is esterified on the two carbonyl groups of the
31 sulfosuccinic molecule and not at the sulfonic group). After stirring for a few minutes, the water

1 layer was extracted with three successive 50 mL portions of dichloromethane, which were
2 combined, dried with anhydrous magnesium sulfate, and evaporated, leaving the desired product
3 (13g, 73% yield). The melting range of the resulting salt was less than about 30°C because the
4 product was a viscous oil at room temperature.

5 [0061] The same experimental procedure was used to prepare ionic liquids of the tetrabutyl
6 ammonium cation with the sodium salts of the following docusate variants: (i) di-n-cyclohexyl
7 ester of sulfosuccinic acid; (ii) di-n-octyl ester of sulfosuccinic acid; (iii) di-n-butyl ester of
8 sulfosuccinic acid; (iv) di-isobutyl ester of sulfosuccinic acid; (v) di-neopentyl ester of
9 sulfosuccinic acid; (vi) di-n-heptyl ester of sulfosuccinic acid; and (vii) di-n-heptyl ester of
10 sulfosuccinic acid. The melting range of the resulting salts was less than about 80°C and
11 typically between about 40°C and 80°C. The octyl and heptyl docusate variants had lower
12 melting ranges as indicated by the fact that they were a viscous liquids at room temperature.

13 [0062] **Representative NMR Data**

14 [0063] The structure and composition of the ionic liquids was determined by $^1\text{H-NMR}$
15 spectroscopy. For all docusate salts (2-ethylhexylsulfosuccinate diester), the spectra consist
16 simply of resonances arising from the anion superimposed on those of the cation. For all
17 docusate salts, resonances originating from the anion were (with minor variations) within the
18 following ranges: (300 Mhz, CDCl_3 , d): 0.73-0.83 (triplets), 1.24-1.70 (overlapping multiplets),
19 3.05-3.31 (complex m), 3.90-4.25 (overlapping m)

20 [0064] Cation resonances (300 MHz, CDCl_3 , d): (1-methyl-3-hexyl imidazolium): 0.79 (t),
21 1.21-1.27 (overlapping m), 1.80 (m), 4.03 (s), 4.22 (t), 7.35 (s), 7.49 (s), 9.50 (s).

22 [0065] (tetraethylammonium): 1.32 (t), 3.34 (q)

23 [0066] (tetrabutylammonium): 1.03 (t), 1.20-1.40 (overlapping m), 3.23 (q)

24 [0067] (tetraoctylammonium): 0.86 (t), 1.18-1.50 (overlapping m), 3.25 (q)

25 [0068] (N-methyl-N-($\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_3$)pyrrolidinium): 0.86 (t), 1.31 (m), 2.11 (m), 3.0-
26 4.2 (complex overlapping m)

27 [0069] (trimethylhexadecylammonium): 0.87 (t), 1.20-1.60 (overlapping m), 2.13 (s), 3.15
28 (q)

29 [0070] (methyltributylammonium): 0.84 (t), 1.23-1.70 (overlapping m), 2.20 (s), 3.24 (m)

30 [0071] (1,2-bis(tributylammonium)ethane): 0.83 (t), 1.22-1.58 (overlapping m), 2.20 (s),
31 3.22 (m)

1 [0072] Ionic liquids of several docusate variants were also made. The NMR spectra of these
2 salts, like those of the docusate derivatives, consist of the spectrum of the specific anion
3 overlayed on that of the specific cation. Below are the NMR data for the tetrabutylammonium
4 derivatives of three docusate variant salts. For each salt, the resonances arising from the cation
5 comport with those of the tetrabutyl ammonium cation of docusate, the values for which are
6 listed above. Below are the resonances from the anion of these example salts (300 MHz, CDCl₃,
7 d):

8 [0073] Bis (n-hexylsulfosuccinate diester): 0.84 (t), 1.2-1.4 (overlapping m), 1.6 (m), 3.07
9 (m), 4.05-4.22 (overlapping m).

10 [0074] Bis (cyclohexylsulfosuccinate diester): 1.2-1.8 (complex overlapping m), 3.10 (m),
11 4.2-4.8 (overlapping m)

12 [0075] Bis (neopentylsulfosuccinate diester): 0.87 (s), 0.90 (s), 3.05-3.25 (overlapping m),
13 3.78 (s), 3.80-3.93 (m), 4.23-4.29 (m)

14 [0076] Bis (N-ethyl-N-(2-ethylhexyl)sulfosuccinate diamide): 0.75-0.88 (triplets), 1.21-1.78
15 (overlapping multiplets), 2.24 (m) 3.11-3-41 (complex m), 3.86-4.45 (overlapping m)